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G6R R7

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EP 0610153 A1 EP 0138289 A1 EP 0073366 A2

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ONLINE DATABASE:WPI

(54) Decontamination of metals

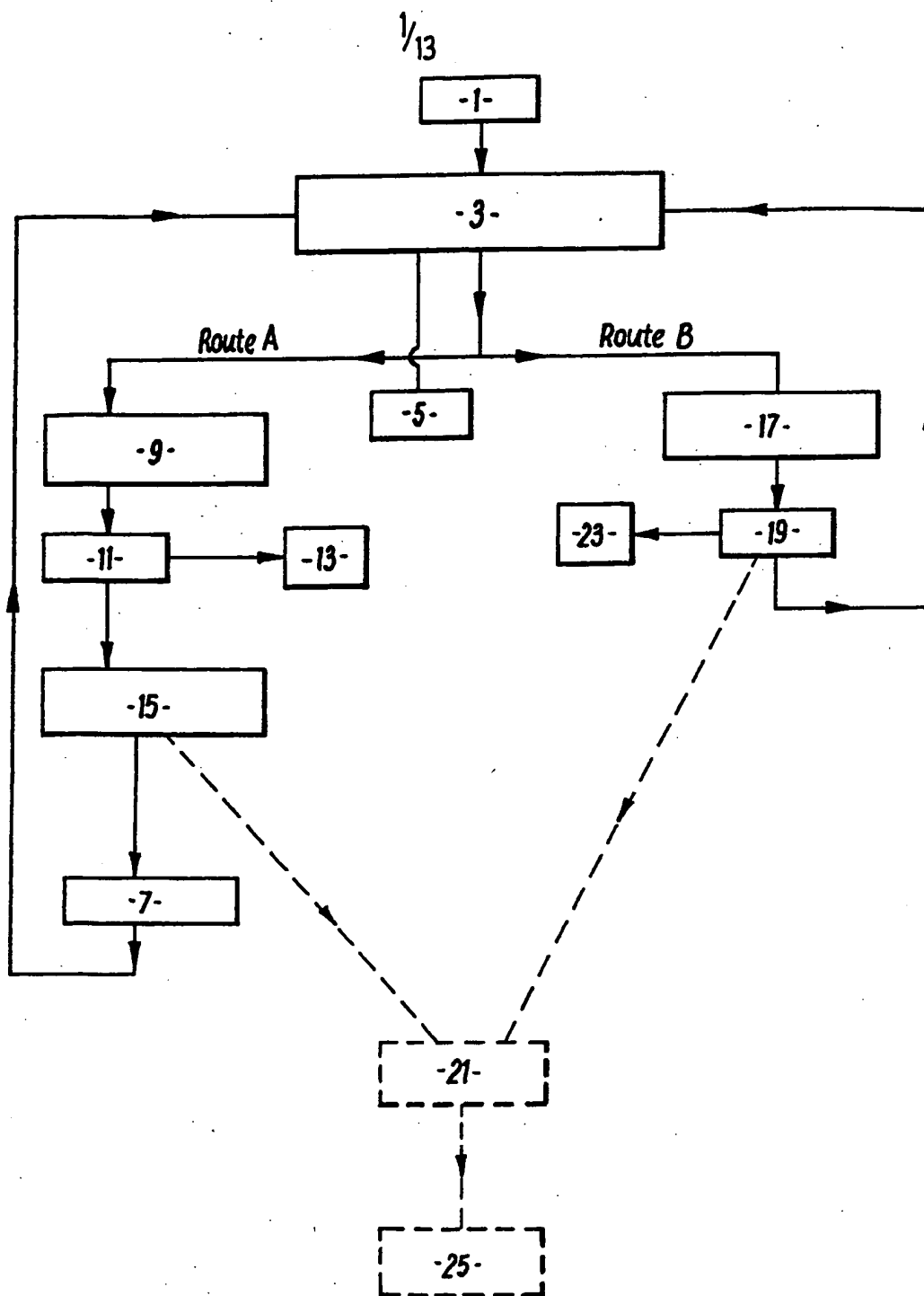
(57) A process for the decontamination of a metallic material, especially a lead or iron containing material, comprises contacting the material with a decontaminant reagent solution which comprises an organic acid to dissolve a contaminated layer of the material in the reagent solution to form an organic metal compound, oxidising the metal compound to form a precipitate with which the contaminants are associated and separating the precipitate from the reagent solution containing it.

The organic acid preferably comprises formic acid although it may also comprise one or more other known acid solvents, eg acetic acid, trifluoroacetic acid, citric acid or oxalic acid with or without other solvent, eg formaldehyde.

Any contaminants associated with the metal which is dissolved will no longer be supported by the metal and in most cases the contaminants will themselves dissolve in the reagent solution.

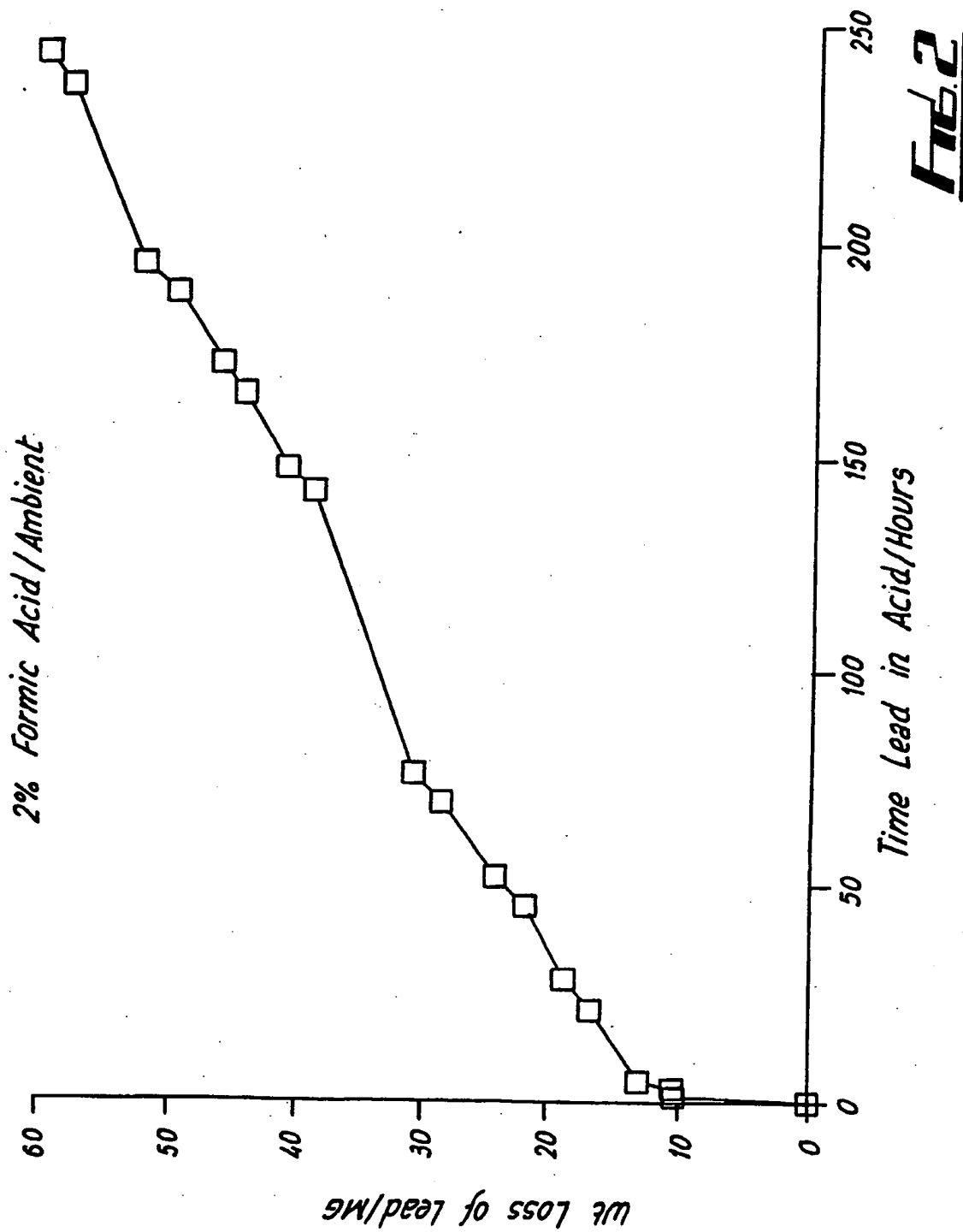
The oxidation may be achieved chemically using eg. hydrogen peroxide or may be carried out electrochemically.

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**FIG. 1**

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5% Formic Acid/Ambient

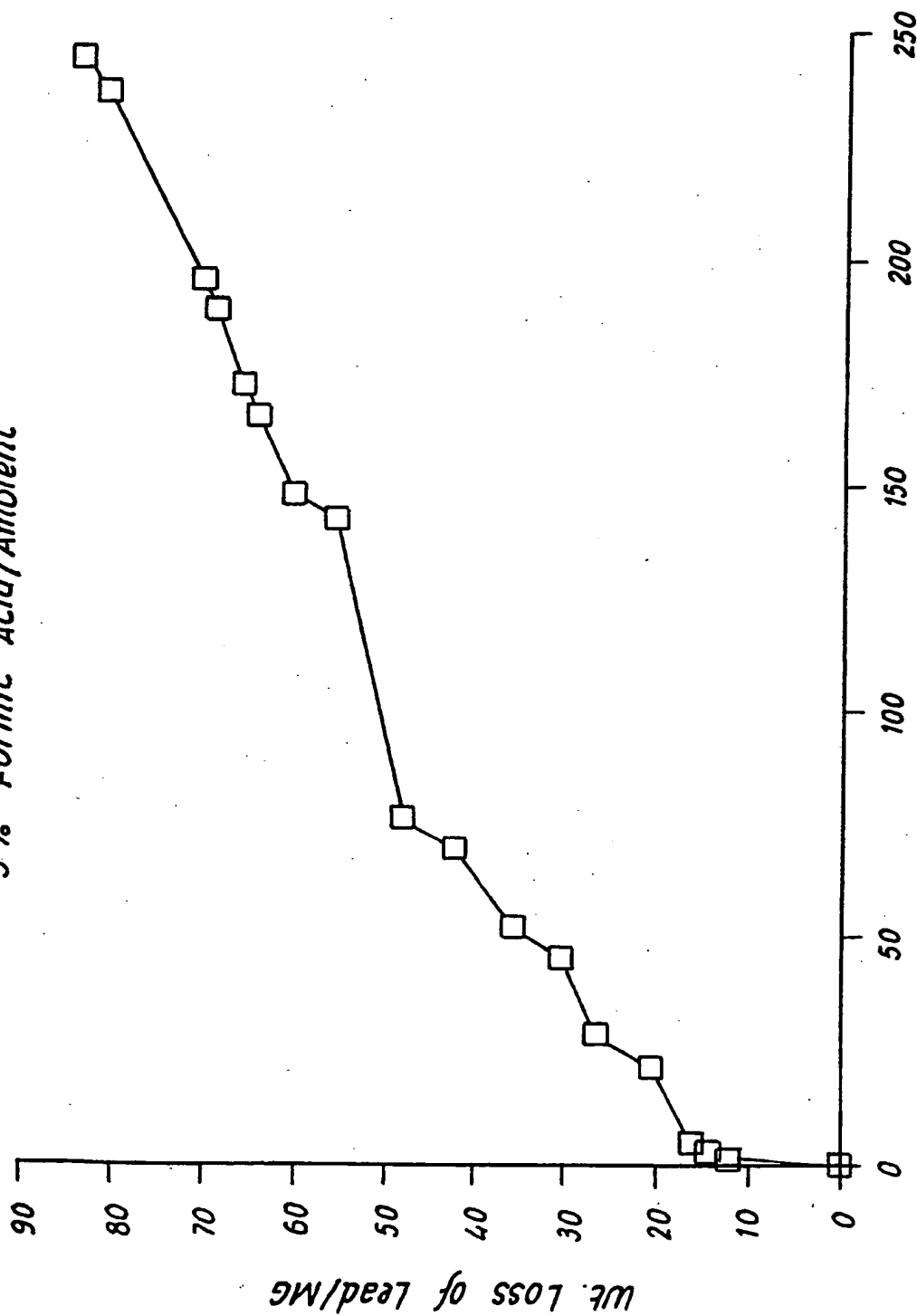
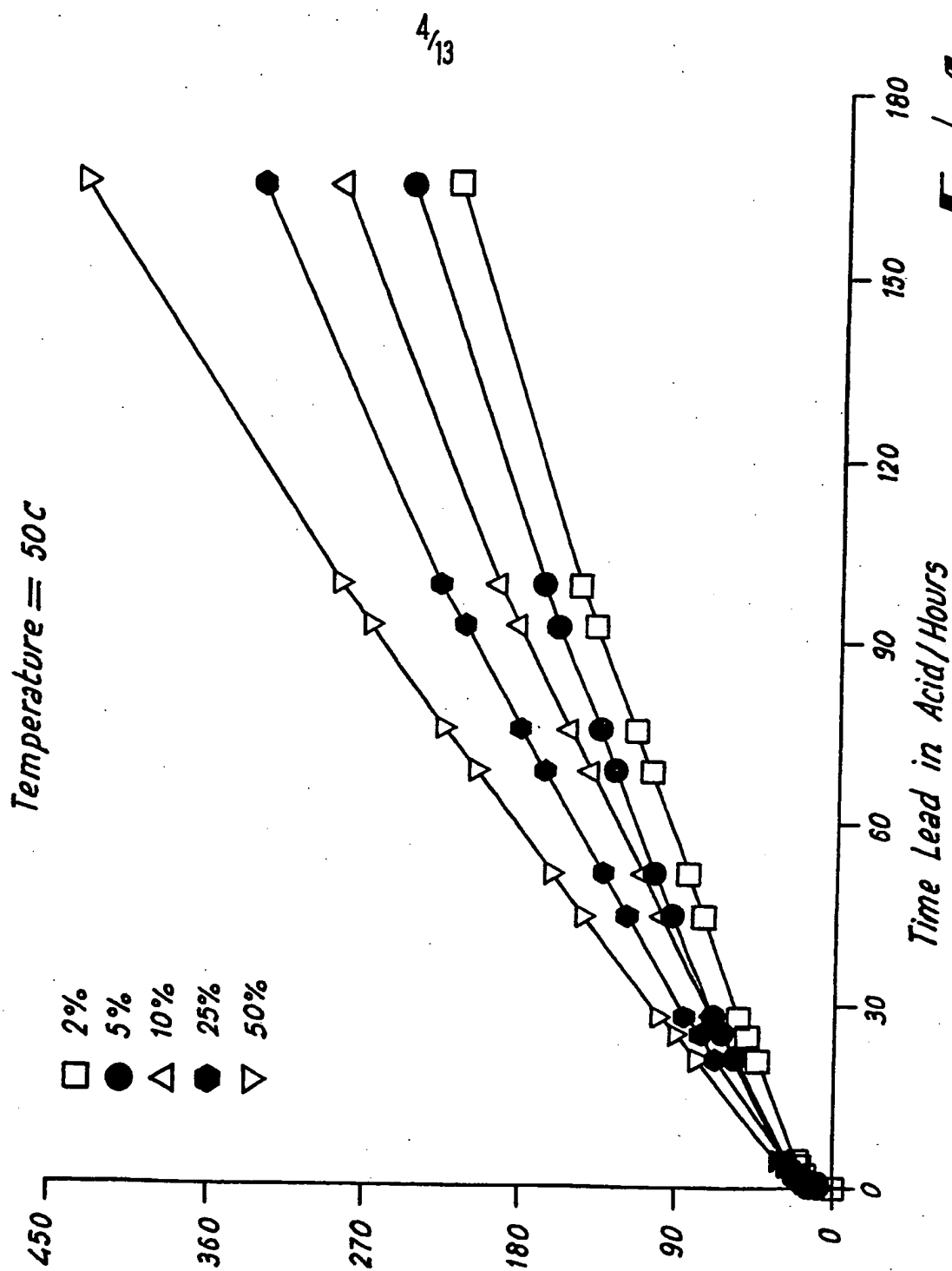


Fig. 3



**Fig. 4**

2% Formic Acid/80 C

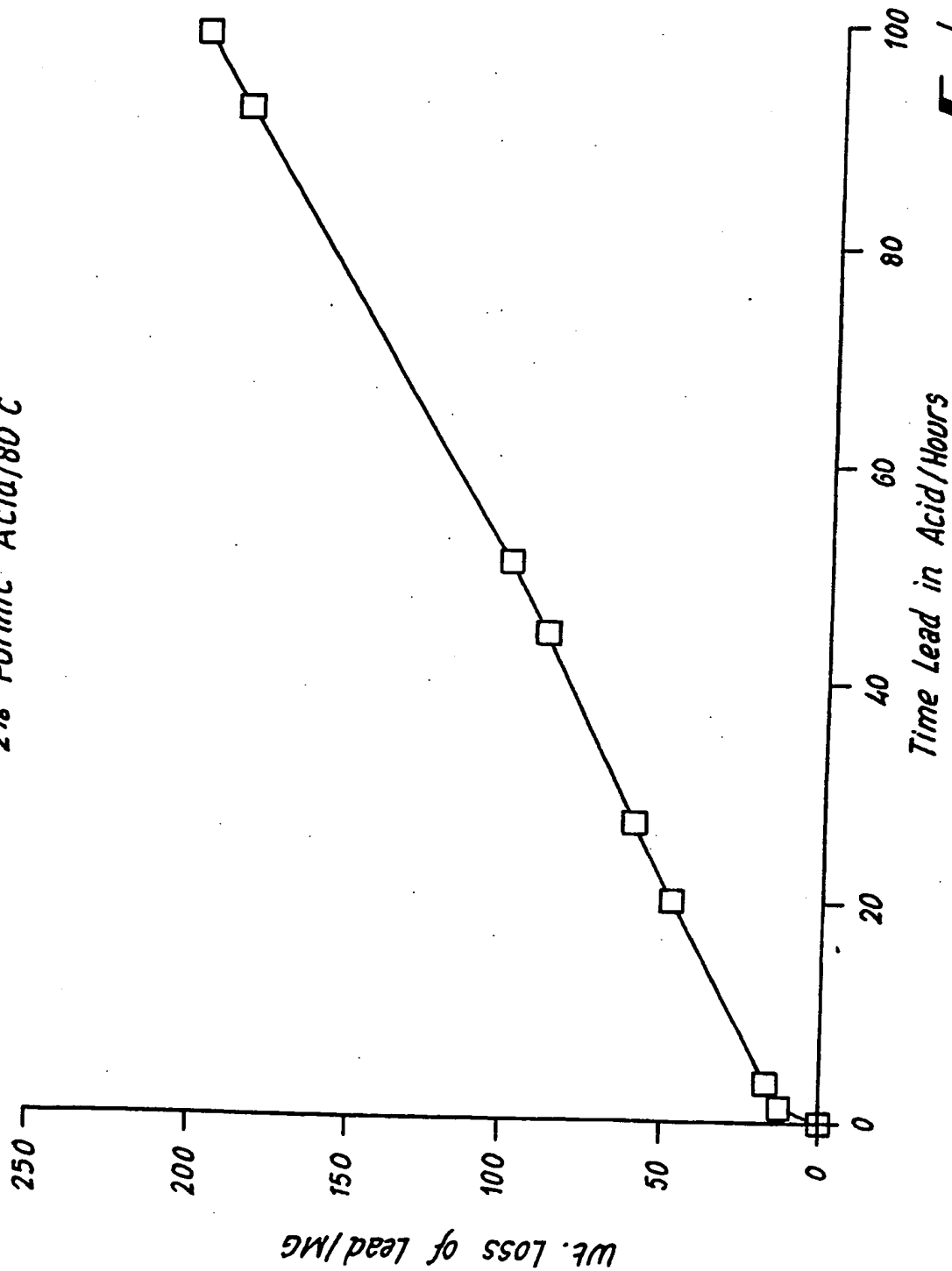
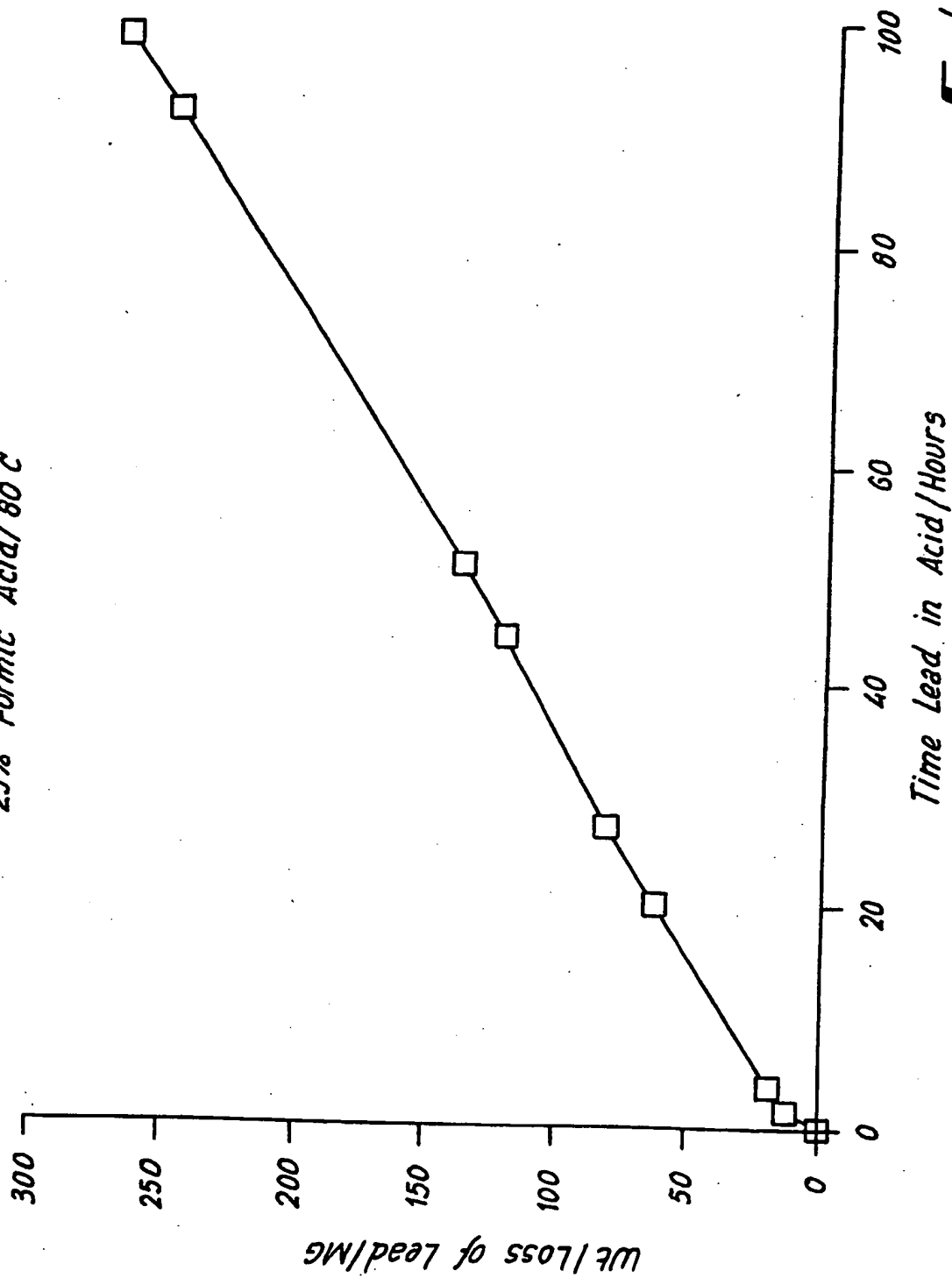


Fig. 5

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25% Formic Acid/80 C



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**Fig. 6**

25% Formic Acid / 1% H<sub>2</sub>O<sub>2</sub> : 80°C

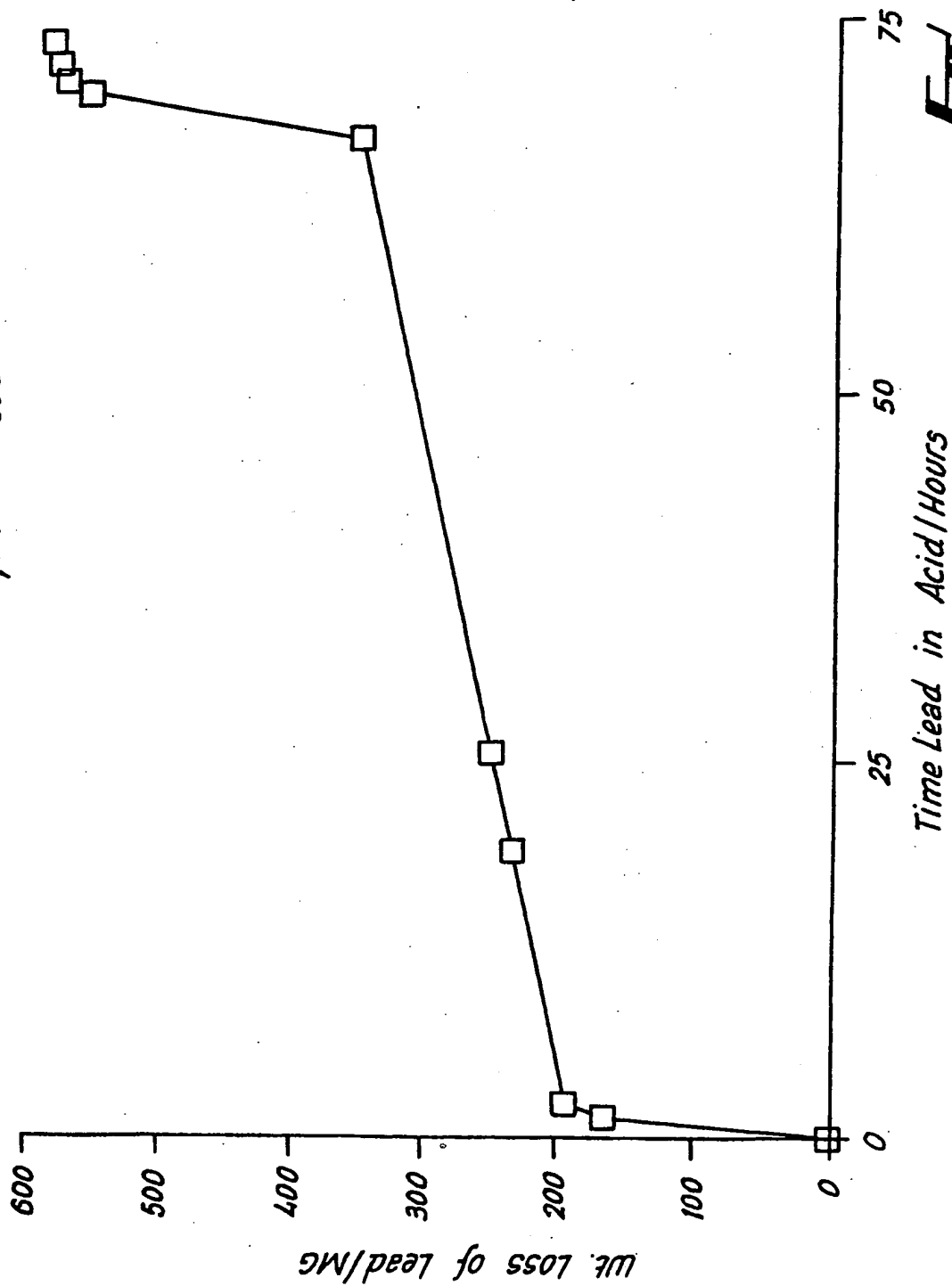
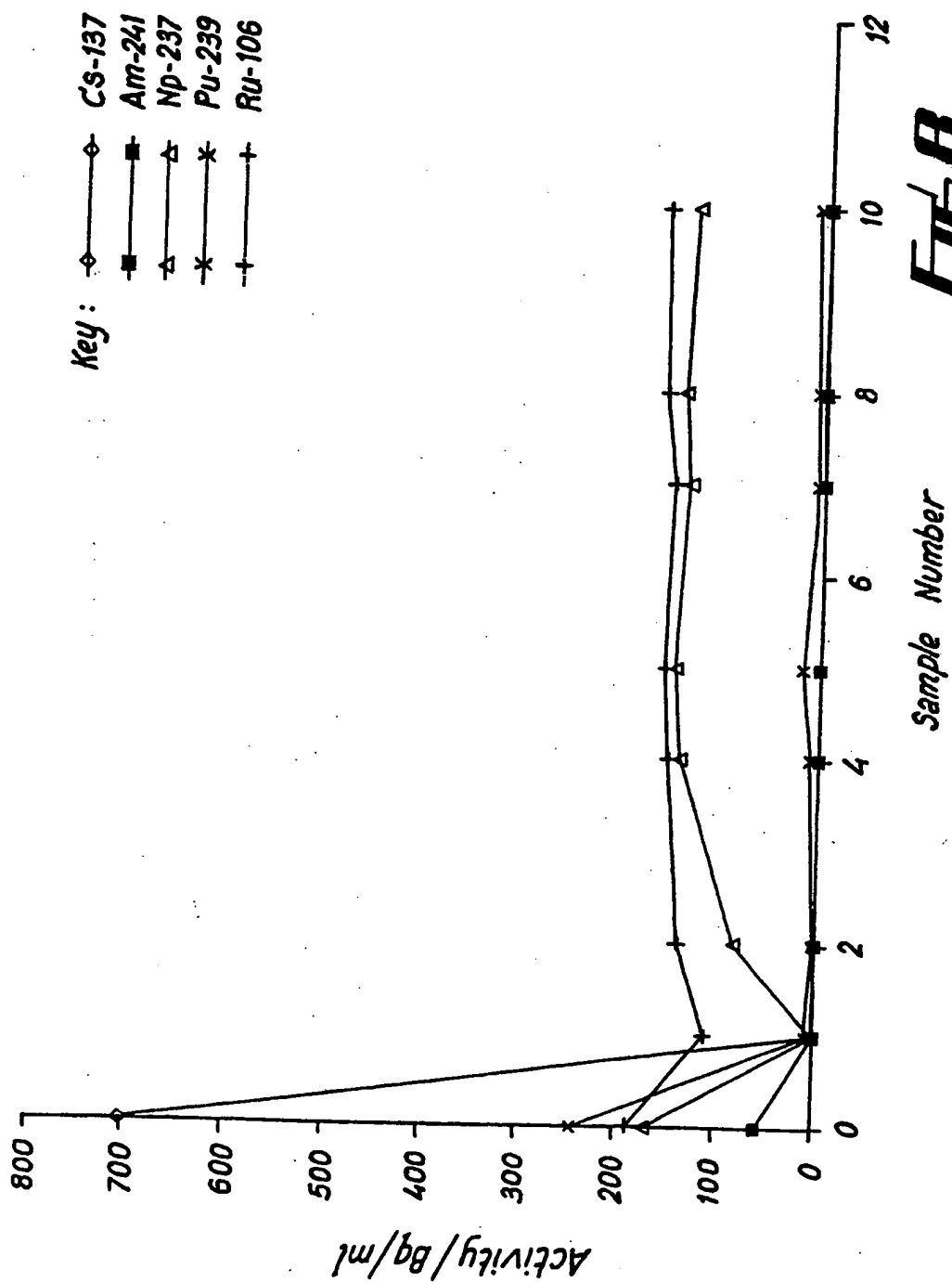


Fig. 7

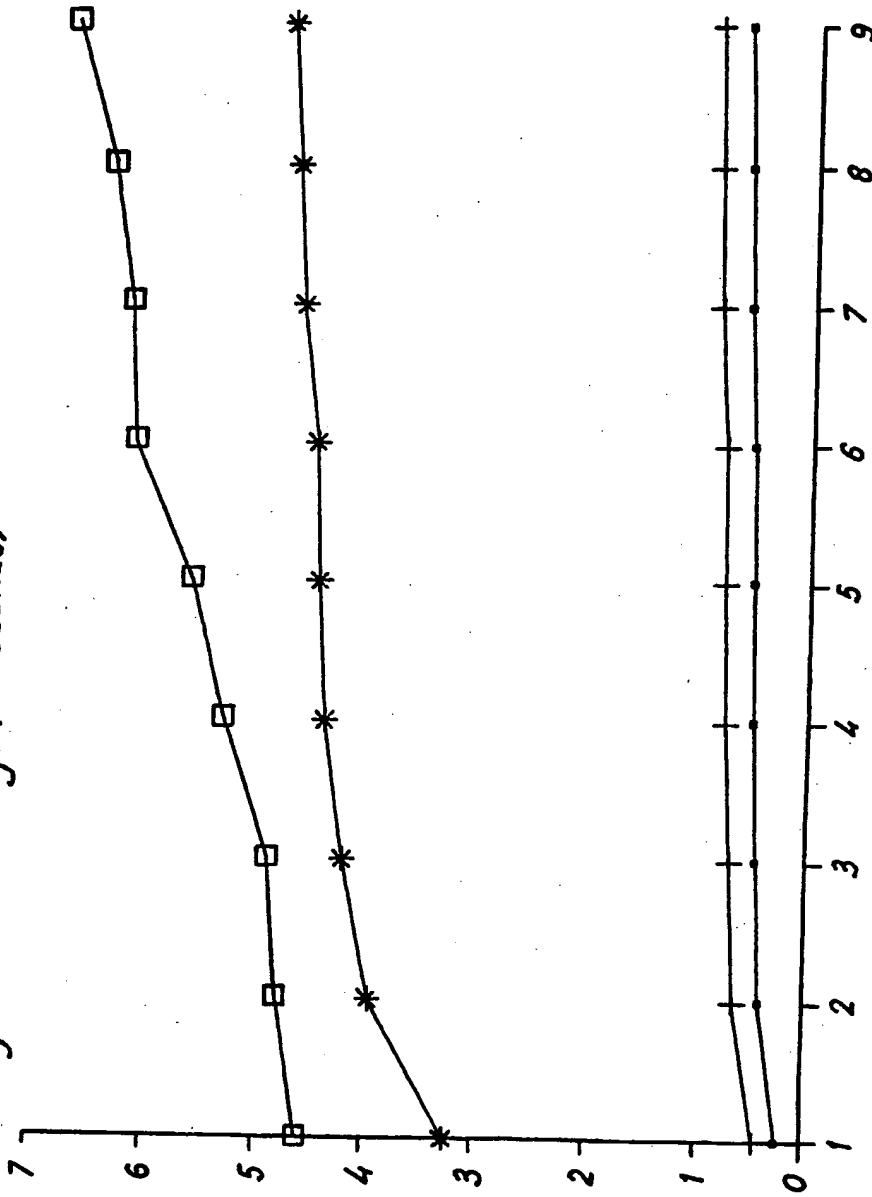


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**Fig. 8**

Weight Loss in mg. (Thousands)



Time Hours

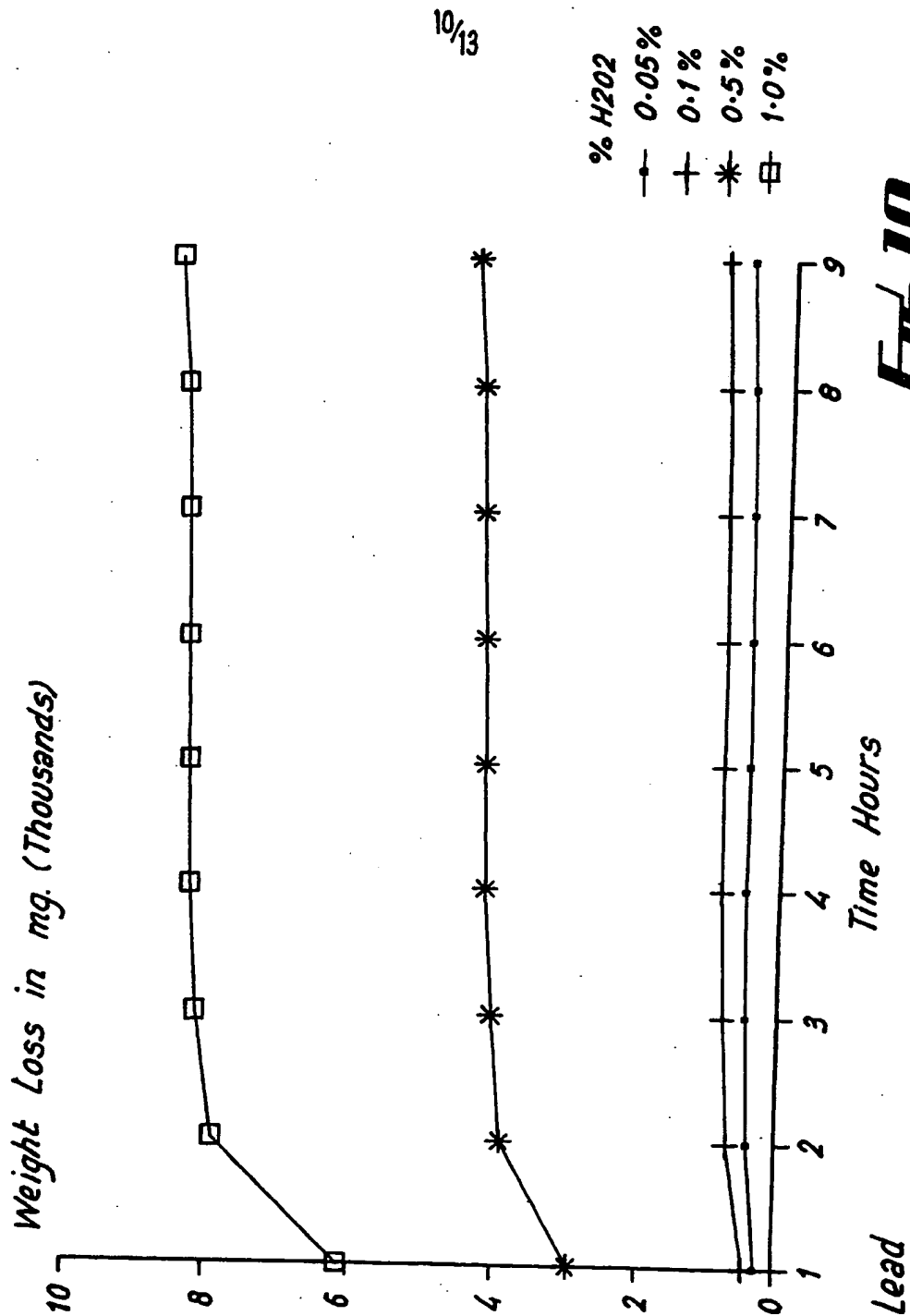
Lead

**Fig. 9**

% H2O2

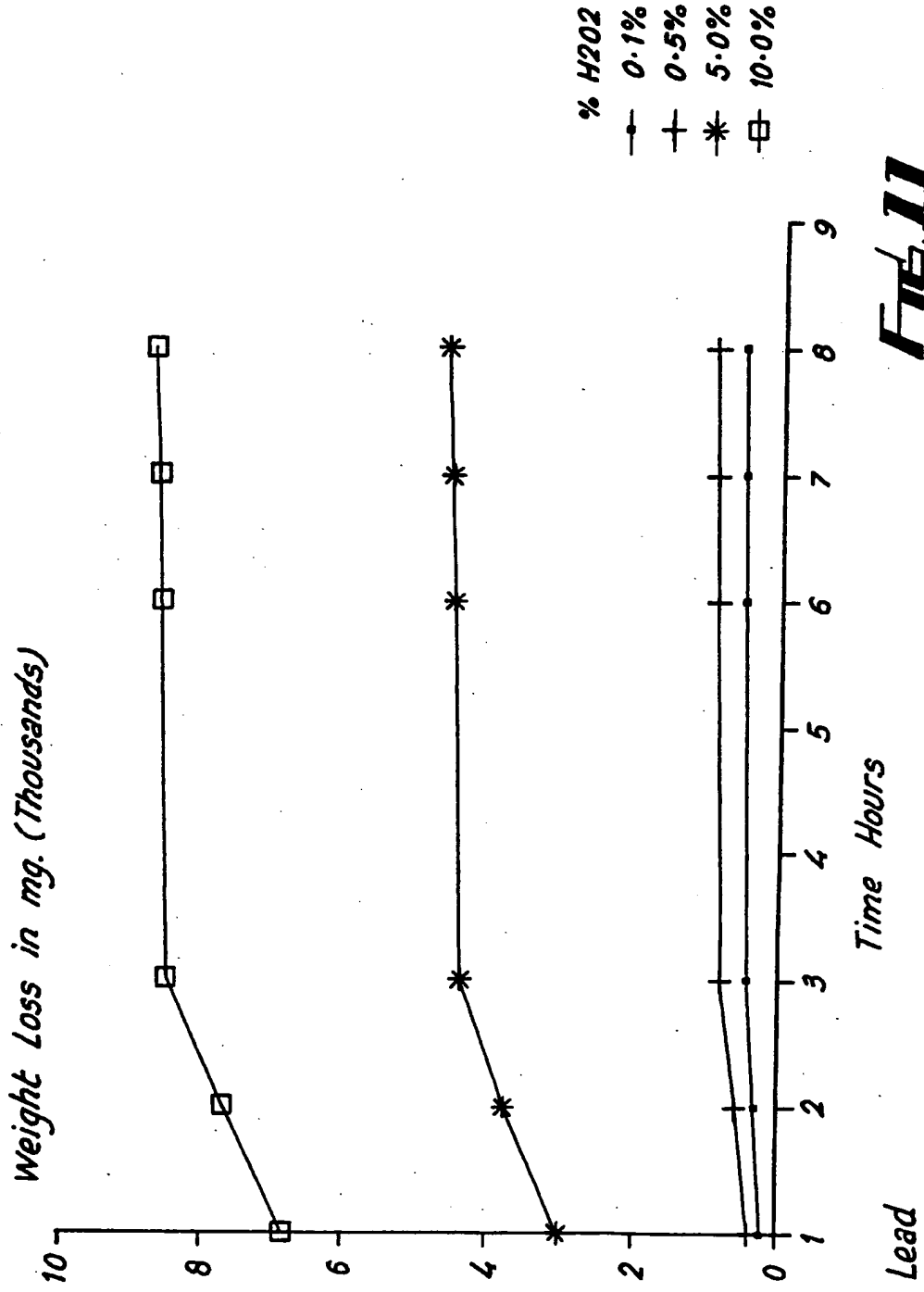
- 0.05%
- 0.1%
- 0.5%
- 1.0%

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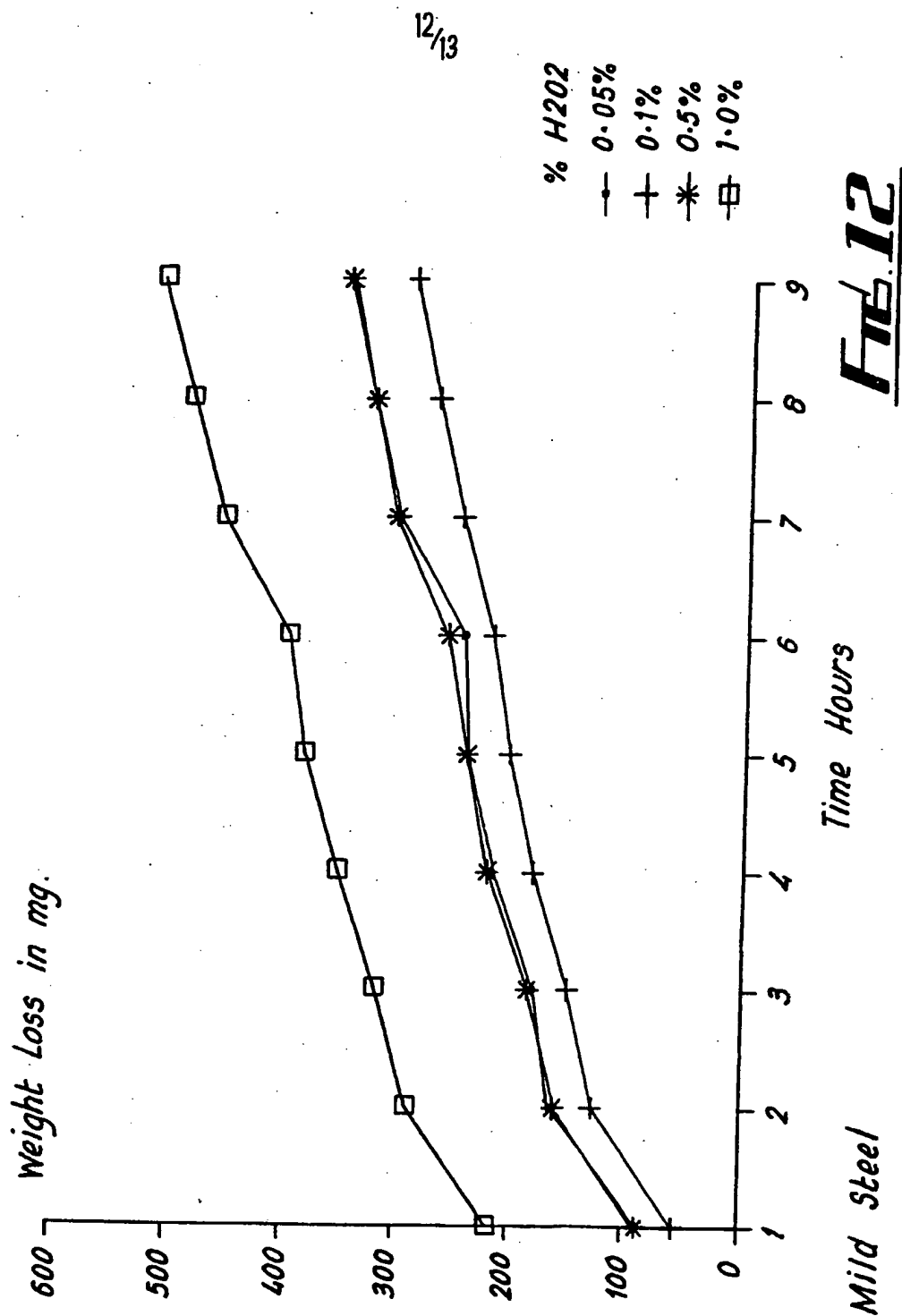


**Fig. 10**

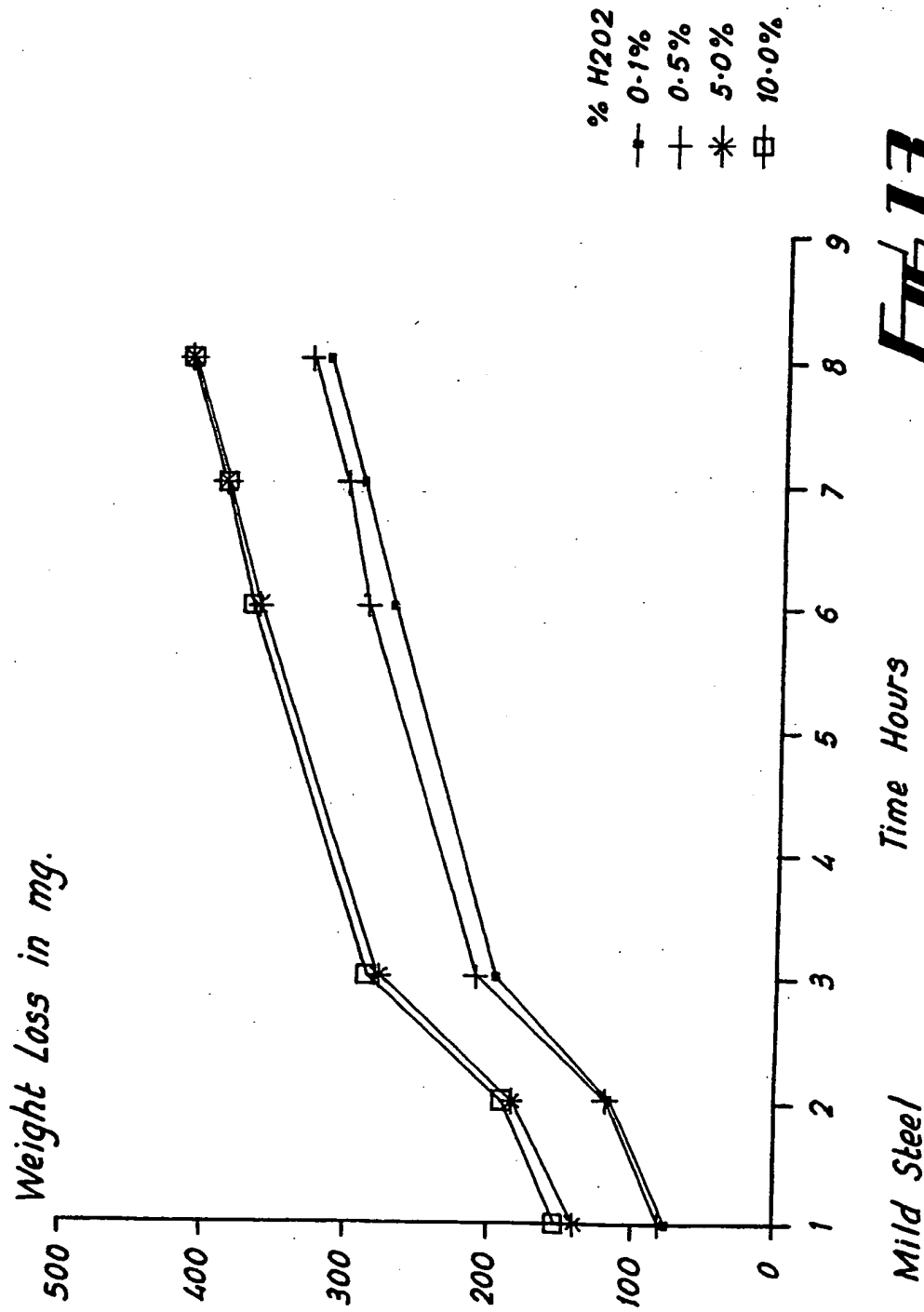
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**Fig. 11**



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**Fig. 13**

DECONTAMINATION OF METALS

The present invention relates to the decontamination of metals in particular lead-containing or iron-containing metals.

Lead is widely used as a shielding material in nuclear materials processing, reprocessing and storage facilities and large quantities of lead develop surface contamination of radionuclides and require treatment to remove such contaminants. Similarly, iron is used widely for constructional purposes and decontamination of iron structures and components is a process frequently used in the nuclear industry,

According to the present invention there is provided a process for the decontamination of a metallic material which comprises contacting the material with a decontaminant reagent solution which comprises an organic acid to dissolve a contaminated layer of the material in the reagent solution to form an organic metal compound, oxidising the metal compound to form a precipitate with which the contaminants are associated and separating the precipitate from the reagent solution containing it.

The organic acid preferably comprises formic acid although it may also comprise one or more other known acid solvents, eg acetic acid, trifluoroacetic acid, citric acid or oxalic acid with or without other solvent, eg formaldehyde.

Where the organic acid provides a monovalent radical and the substrate material to be treated comprises lead, the molar concentration of acid employed is desirably at least equivalent to twice the molar concentration of lead to be removed from the material to be decontaminated.

Any contaminants associated with the metal which is dissolved will no longer be supported by the metal and in most cases the contaminants will themselves dissolve in the reagent solution.

The oxidation may take place at the same time as the contaminated metal dissolution thereby assisting the kinetics of that process as well as after the dissolution to form the said precipitate and may be effected by use of a chemical oxidising agent, eg a peroxide such as hydrogen peroxide or potassium permanganate, or by an electrochemical process.

During the metal dissolution the organic acid if not in excess may be virtually all consumed and further organic acid may be added or chemical treatment may be applied chemically or electrochemically to yield the requisite contaminant-containing precipitate and optionally to regenerate the organic acid.

The treatment where applied subsequently may for example be effected by a mineral acid, eg a concentrated acid such as sulphuric or hydrochloric acid solution. Such an acid not only precipitates lead as either a sulphate or chloride but also regenerates organic acid.

The precipitate and associated contaminants may be separated from the solution from which they have been precipitated by filtration or any other suitable process, eg using a hydrocyclone. After separation the precipitate and contaminants may be encapsulated and disposed of in a known way, eg as a cementitious residue.

After extraction of the precipitate and contaminants, any remaining or regenerated organic acid reagent solution may be recycled and re-used where necessary by mixing with a fresh supply of organic acid containing reagent. The solution may be further purified before such re-use, eg by a known process such as ion exchange.

The present invention beneficially provides a process for decontaminating metallic material, especially lead or iron, which can be operated without producing undesirable liquid effluents which are costly to treat prior to release to the environment.



The only significant waste stream is a precipitate of lead compounds and associated contaminants eg radionuclides, in a volume corresponding to the volume of surface layers removed from the treated substrate.

The decontamination reagent liquid effluent can be reused in subsequent decontamination cycles having been cleaned of dissolved metal ions and contaminants during the precipitation/separation step.

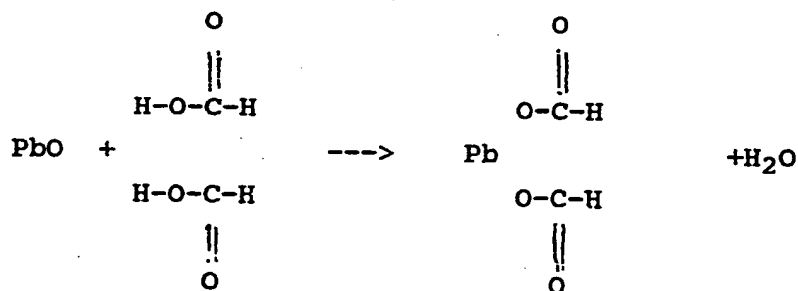
Addition of the oxidising agent such as  $H_2O_2$  to the organic acid increases the kinetics of metal dissolution reaction, such that very low concentrations of decontaminant can be used in the reaction vessel. The advantage of using low concentrations of a reusable aqueous decontaminant lies in the ability to remove surface layers and contamination from a substrate at a carefully controlled rate, without incurring a penalty in terms of increased secondary wastes. By carefully controlling the rate of removal of contaminants the level of radiation in the waste stream can be controlled to ensure that human operators' radiation dose uptake is maintained at an acceptable minimum without the requirement for heavy shielding or expensive remotely operated facilities. This process therefore is suitable to be applied using mobile apparatus which may conveniently be transported to the site where decontamination is required. At such sites the process may be used even though liquid effluent discharge routes may not be available and where the use of heavy shielding/remote equipment may be prohibited for reasons of weight and cost.

In the process according to the present invention contaminated metal components, eg blocks, strips or sheets of metallic material, may, after being assayed for radionuclide inventory, be introduced into a reaction vessel. The vessel is charged with decontamination reagent at a molar concentration equivalent to twice the

molar concentration of lead to be removed from the surface of the substrate. The molar concentration to be removed is calculated from the amount of metal surface to be removed to satisfy the decontamination target, against the maximum inventory of radionuclides permissible in the resultant waste stream, to ensure that radiation exposure of human operators is minimised. By this procedure it is possible to limit the capacity of the decontaminant reagent to take up lead and contaminants by using a restricted molar quantity of decontaminant reagent in the reaction vessel. As noted above, addition of oxidising agent increases the kinetics of the reaction facilitating the use of dilute solutions to control radiation dose in the resultant waste stream.

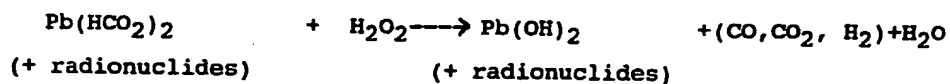
Where the metal comprises lead, the organic acid comprises formic acid and the oxidising agent comprises hydrogen peroxide the following reactions illustrate the chemical processes which take place:

(A) Dissolution of lead in formic acid



2 moles Formic acid react with 1 mole of Lead.

(B) Precipitation



Conveniently, the process according to the present invention may be carried out in a transportable apparatus which may be transported to and used at different sites where lead decontamination has to be carried out.

Embodiments of the present invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a schematic flowsheet diagram illustrating a process for the decontamination of lead.

Figures 2 to 7 are graphs illustrating dissolution of lead samples in formic acid solution in the process illustrated in Figure 1 as follows:

Figure 2 is a graph of weight loss of lead sample versus time in 2 per cent formic acid solution at ambient (room) temperature.

Figure 3 is a graph of weight loss of lead sample versus time in 50 per cent formic acid solution at ambient temperature.

Figure 4 is a graph of weight loss of lead samples versus time in formic acid solutions of different concentrations (2%, 5%, 10%, 25% and 50% as indicated in the key to the Figure) all at a temperature of 50C.

Figure 5 is a graph of weight loss of lead sample versus time in 2 per cent formic acid solution at a temperature of 80C.

Figure 6 is a graph of weight loss of lead sample versus time in a 25 per cent formic acid solution at a temperature of 80C.

Figure 7 is a graph of weight loss of lead sample versus time in a 25 per cent formic acid solution together with 1%  $H_2O_2$  at a temperature of 80C.

Figure 8 is a graph of radioactivity against sample number for various purified liquid samples taken in the process illustrated in Figure 1.

Figure 9 is a graph of weight loss of the lead sample treated by the process illustrated in Figure 1 versus time

for a 0.5% formic acid solution with various solution concentrations of  $H_2O_2$  added..

Figure 10 is a graph of weight loss of the lead sample treated by the process illustrated in Figure 1 versus time for a 1.0% formic acid solution with various solution concentrations of  $H_2O_2$  added.

Figure 11 is a graph of weight loss of the lead versus time for a 5.0% formic acid solution with various solution concentrations of  $H_2O_2$  added.

Figure 12 is a graph weight loss versus time for a mild steel component contacted by a 1.0% formic acid solution with various concentrations of  $H_2O_2$  added.

Figure 13 is a graph of weight loss versus time for a mild steel component contacted by a 5.0% formic acid solution with various concentrations of  $H_2O_2$  added.

In the process illustrated in Figure 1 samples of lead to be decontaminated are first inspected in an inspection stage 1 to determine the thickness of surface metal which needs to be removed. The sample may be inspected visually and/or by using remote inspection techniques. This allows the depth of radioactive contamination and the extent of contamination to be determined. The sample is next passed to a contacting stage 3 where it is immersed in a bath of a decontaminant reagent solution under oxidising conditions as described above. The process conditions in the contacting stage 3 are determined by reference to the amount of lead desired to be removed from the sample which is known from the result of the inspection in the inspection stage 1. In due course, after a sufficiently thick layer of lead and contaminants has been dissolved in the reagent solution the remaining lead is removed and may be washed, re-cycled and reused as indicated at stage 5.

The further treatment of the reagent solution containing dissolved lead and contaminants follows either Route A shown on the left hand side of Figure 1 or Route B shown on the right hand side of Figure 1. Route A

represents the route in cases in which the lead sample in stage 1 was determined to be highly contaminated. Route B represents the route in cases when the lead sample in stage 1 was determined to have only low contamination.

In Route A, the lead- and contaminant-containing reagent solution is further oxidised as indicated at stage 9 to yield a precipitate of lead hydroxide and radioactive contaminants. In practice, the further oxidation may take place in the same reactor vessel as the contacting stage 3. The precipitate is removed in a suitable separation process, eg filtration, as indicated at stage 11. The solid filtrate may be encapsulated and disposed of in a known way in a disposal treatment stage 13. The cleaned reagent solution is recirculated via a further treatment stage 15 to a reagent mixing stage 7. In the further treatment stage 15 the recycled reagent solution may be further purified, eg by ion exchange, in a known way. In the mixing stage 7 the reagent solution is combined with reagent from a fresh supply 19 for re-use in the contacting stage 3.

In Route B the lead- and contaminant- containing reagent solution is treated in a stage 17 with a mineral acid solution comprising either concentrated sulphuric acid or hydrochloric acid solution. This causes lead and contaminant precipitation and organic acid regeneration. The precipitate is thereafter separated in a separation stage 19 and the precipitate is treated and disposed of in a precipitate treatment stage 23. The remaining reagent solution is recirculated to the stage 3.

When it is desired to close down the cycle of operations, eg after all use at a particular site, the final supply of circulating decontamination reagent may be removed by use of an evaporator 21 indicated by dashed lines in Figure 1 followed by close down 25.

In order to demonstrate the dissolution of lead in formic acid using the process described above especially

stage 3 of that process the following illustrative example experiments were carried out.

Lead block samples were prepared by roughening of the lead surfaces followed by washing of the samples with purified water and then drying, in order to remove any loosely attached lead on the block. The dimensions of each lead block used were recorded (in mm) in order to calculate the total surface area in contact with the acid when immersed. The lead blocks were weighed accurately after drying and then immersed separately in 100ml solutions of formic acid of known concentration, in a round-bottomed flask. The temperature was variably controlled by immersing each of the flasks in a water bath. Different dissolutions runs were thereby carried out at different temperatures and acid concentrations.

The following further steps were taken.

(a) Cotton-wool was used as a seal at the top of each flask to prevent the loss of acid due to evaporation at the high temperature.

(b) Each lead block was weighed at hourly and then two hourly intervals for the first day. Weights were then recorded twice daily.

In one of the dissolution runs  $\text{H}_2\text{O}_2$  was added to the formic acid solution.

All the results were collected and recorded in tables for each dissolution run with the weight loss of the lead block being recorded at each time interval. Selected graphs were constructed illustrating the results obtained and these are shown in Figures 2 to 9.

It is noticeable from the graphs of weight loss versus time shown in Figure 2 to 7 that during the first few hours (for all the runs carried out) the outer surface of the lead block was dissolved at a greater rate than for the remainder of the experiment. This may possibly be due to the removal of an oxide layer from the surface of the lead. However, after the removal of the surface layer,

dissolution of the lead for each run continued at a constant rate.

The graphs of weight loss versus time at ambient temperature, Figures 2 and 3, show gradients which alter slightly at certain periods of time. This was due to the fact that the dissolution runs continued during the night when the temperature dropped, thus decreasing the dissolution rate (gradient of the line on the graph decreasing). This was for runs carried out in air rather than in the water bath; thus cell temperature correlated with ambient temperature of the room for such runs. During the day, however the acid temperature maintained an average of 19.5°C, increasing the gradient of the lines constructed on the graphs.

It is clear from Figures 2 to 9 that the dissolution rate for lead in formic acid increased with an increase in temperature and also with an increase in acid concentration.

The presence of  $H_2O_2$  in formic acid had a considerable effect on the dissolution rate of the lead block, as can be seen from a comparison of Figures 6 and 7. During the first hour the dissolution rate with  $H_2O_2$  in acid (Figure 7) was considerably higher than for the equivalent run of lead in the same concentration (25%) acid only (Figure 6). However, after about two hours the dissolution rate in Figure 7 decreased to a much lower rate. Another 1ml sample of  $H_2O_2$  was added to the formic acid after 71.5 hours and again, as can be seen from Figure 7, the dissolution rate increased considerably at this point. It can therefore be assumed that all of the  $H_2O_2$  was consumed within about the first two hours after the run was started and clearly it has a considerable effect on the dissolution rate of lead in formic acid. Further  $H_2O_2$  added assisted the dissolution rate.

Figure 8 illustrates use of an inorganic ion exchange column as the treatment stage 15 in the process depicted

in Figure 1. The activity of certain radionuclides in the formic acid/H<sub>2</sub>O<sub>2</sub> solution eluent leaving such a column is sampled hourly. Curves A, B, C, D, E represent the activity detected from the presence respectively of Cs-137, Am-241, Np-237, Pu-239 and Ru-106. As is seen in Figure 8, the concentration of Cs-137, Pu-239 and Am-241 is significantly reduced and the concentration of the other radionuclides is also slightly reduced.

Figures 9 to 11 illustrate for formic acid solutions of various formic acid concentrations that the concentration of H<sub>2</sub>O<sub>2</sub> in the same solution effects an increase in the dissolution of lead.

In Figure 9 the HCOOH concentration is 0.5% by volume. The lead dissolution curves obtained for addition of 0.05%, 0.1%, 0.5% and 1% by volume of H<sub>2</sub>O<sub>2</sub> are curves A, B, C and D respectively.

In Figure 10 the HCOOH concentration is 1% by volume. The lead dissolution curves obtained for addition of 0.05%, 0.1%, 0.5% and 1% by volume of H<sub>2</sub>O<sub>2</sub> are curves A, B, C and D respectively.

In Figure 11 the HCOOH concentration is 5% by volume. The lead dissolution curves obtained for addition of 0.01%, 0.5% and 10% by weight are curves A, B, C and D respectively.

As illustrated in Figures 9 to 11, dissolution of lead increases with increasing H<sub>2</sub>O<sub>2</sub> concentration for each of the three formic acid concentrations.

Steel components may be decontaminated in a manner similar to the process depicted by Figure 1. Figures 12 and 13 illustrate the effect of treating the surface of a mild steel component with a solution of formic acid containing H<sub>2</sub>O<sub>2</sub>.

In Figure 12 the HCOOH concentration is 1.0% by volume. The mild steel dissolution curves obtained for addition of 0.05%, 0.1%, 0.2% and 1.0% by volume of solution are curves A, B, C and D respectively.



In Figure 13 the  $\text{HCOOH}$  concentration is 5.0% by volume. The mild steel dissolution curves obtained for addition of 0.1%, 0.5%, 5.0% and 10% by volume of solution are curves A, B, C and D respectively.

Figures 12 and 13 show that dissolution of mild steel increases with increasing  $\text{H}_2\text{O}_2$  concentration for the two formic acid concentrations.

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Claims

1. A process for the decontamination of a metal-containing material which comprises contacting the material with a decontaminant reagent solution which comprises an organic acid to dissolve a contaminated layer of the material in the reagent solution to form an organic metal compound, oxidising the organic metal compound to form a precipitate with which the contaminants are associated and separating the precipitate from the reagent solution containing it.
2. A process as in Claim 1 and wherein the organic acid comprises one or more of formic acid, acetic acid, trifluoroacetic acid, citric acid and oxalic acid with or without other solvent.
3. A process as in Claim 1 or Claim 2 and where the metal comprises lead and the organic acid provides a monovalent radical and the molar concentration of acid employed is at least equivalent to twice the molar concentration of lead to be removed from the material to be decontaminated.
4. A process as in Claim 1, Claim 2 or Claim 3 and wherein the oxidation takes place at the same time as the contaminated metal dissolution thereby assisting the kinetics of that process as well as after the dissolution to form the said precipitate.
5. A process as in any one of the preceding Claims and wherein the oxidation is carried out by use of a chemical oxidising agent.
6. A process as in any one of Claims 1 to 5 and wherein the oxidation is carried out by an electrochemical process.
7. A process as in any one of the preceding Claims and wherein further chemical treatment is applied to yield the precipitate and to regenerate the organic acid solution.
8. A process as in Claim 7 and wherein the treatment is effected by addition of a mineral acid.

9. A process as in Claim 8 and wherein the mineral acid comprises concentrated sulphuric or hydrochloric acid solution.
10. A process as in any one of the preceding Claims and wherein the precipitate and associated contaminants are separated from the solution from which they have been precipitated and, after separation, the precipitate and contaminants are encapsulated and disposed of.
11. A process as in Claim 10 and wherein after extraction of the precipitate and contaminants, any remaining or regenerated organic acid reagent solution is recycled and re-used optionally by mixing with a fresh supply of organic acid containing reagent.
12. A process as in Claim 11 and wherein the recycled solution is further purified before re-use.

Relevant Technical Fields

- (i) UK Cl (Ed.N) G6C (CFC), G6R (R1A7, R1C1, R1C2, R7)  
(ii) Int Cl (Ed.6) G21F

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

(ii) ONLINE DATABASE: WPI

Search Examiner  
M J CONLON

Date of completion of Search  
10 FEBRUARY 1995

Documents considered relevant  
following a search in respect of  
Claims :-  
1-12

Categories of documents

- X: Document indicating lack of novelty or of inventive step. P: Document published on or after the declared priority date but before the filing date of the present application.  
Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.  
A: Document indicating technological background and/or state of the art. &: Member of the same patent family; corresponding document.

Category	Identity of document and relevant passages	Relevant to claim(s)
X,E	EP 610153 A1 (DECO-HANULIK) published 10.8.94	1 at least
X	EP 138289 A1 (WESTINGHOUSE) pages 9-10	1 at least
X	EP 73366 A2 (Ges. FORDERUNG FORSCHUNG) pages 12-13, page 16 top	1 at least

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